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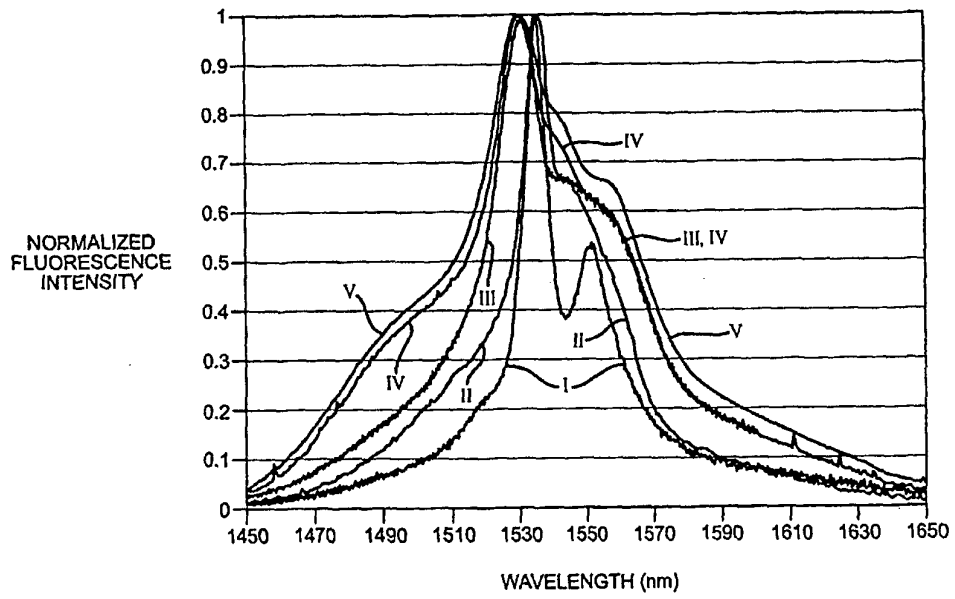
(54) Title: SPCVD SILICATE GLASSES



(57) Abstract

These glasses incorporate a combination of F and Al_2O_3 to achieve even wider fluorescence and improved gain flatness. In addition, SPCVD incorporates large amounts of N into low-loss fiber whose high charge has an impact on rare earth behavior. The Surface Plasma Chemical Vapor Deposition (SPCVD) produces fiber preforms with high levels of F, Al_2O_3, and N. These heavily fluorinated glasses provide much broader Er^{3+} emission than Type I or Type II silica for enhanced multichannel amplifiers. SPCVD successfully fluorinates silica with losses below 5 dB/km and increased Er^{3+} emission width.

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SPCVD SILICATE GLASSES

TECHNICAL FIELD

This invention relates to fluorinated and nitrided silicate glasses made by Surface Plasma Chemical Vapor Deposition. The new glasses are useful for gain flattened Er^{3+} fiber amplifiers. The invention includes making rare earth doped fluorine containing glasses using plasma chemical vapor deposition.

BACKGROUND ART

Er^{3+} doped fiber amplifiers have revolutionized optical telecommunications by providing all-optical high-gain, low-noise amplification without the need for costly electronic repeaters. However, current amplifiers are not well suited for multichannel amplification due to the strong dependence of their gain as a function of wavelength. The fluorinated aluminosilicate glasses provide superior gain flatness in the 1530-1560 nm wavelength band over type I and type II silica. This enables simultaneous uniform amplification of multiple wavelengths for a 4-32x increase in bandwidth in both fiber and planar devices. This also makes high data rate communication systems practical and affordable. For example, 16 channels at 10 Gb/s (OC-192 Standard) for 160 Gb/s^2 or even 32 channels at 2.4 gb/s (OC-48 Standard) for 76.8 Gb/s total capacity are possible.

Recent developments show that fluorinating Er^{3+} doped SiO_2 increases the fluorescence bandwidth emission at 1550 nm. The art also shows that Al_2O_3 additions increase the fluorescence line width and solubility of Er^{3+}.

DISCLOSURE OF INVENTION

Our development incorporates a combination of fluorine, Al_2O_3 and/or Ga_2O_3 to achieve even wider Er^{3+} fluorescence and improved gain flatness in the 1550 nm telecom window. In addition, SPCVD can incorporate large amounts of F, Al_2O_3 and N into low-loss fiber all of which impact rare earth behavior. The SPCVD produces fiber preforms with high levels of fluorine, alumina, and nitrogen. These heavily fluorinated glasses provide much

broader Er^{3+} emission than Type I or Type II silica for enhanced multichannel amplifiers. SPCVD successfully fluorinates silica with losses below 5 dB/km and increased Er^{3+} emission width.

The rare earth doped glass composition of this invention comprise:

Component	Weight Percent
SiO_2	0-95
GeO_2	0-95
Al_2O_3	0-15
Ga_2O_3	0-15
F	2-10
N	0-10
R_2O_3	0.01-2.0

wherein SiO_2 + GeO_2 range from 80-95 wt.%, Al_2O_3 + Ga_2O_3 range from 5-15 wt.%, F range from 2 to 10 wt.% and R_2O_3 is a rare earth oxide. The sums such as SiO_2 + GeO_2 are fully interchangeable. Furthermore, each of SiO_2 and GeO_2 can range from 0-95% as long as the total SiO_2 + GeO_2 is between 80 and 95%.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing the effect of our invention on Er^{3+} fluorescence.

Fig. 2 is a graph showing microprobe compositional data of our fluorinated and nitrated preform.

BEST MODE OF CARRYING OUT INVENTION

Most attempts to fluorine dope alumino silicate soot made by CVD lead to a stripping of Al_2O_3 and GeO_2 due to the high vapor pressures of AlF_3 and GeF_4. These attempts can not achieve F dopant levels above about 2 wt%F. However, SPCVD allows for simultaneous co-doping of high levels of fluorine, up to 5 wt%, and Al_2O_3. This achieves an even greater fluorescence line width and increased rare earth solubility. The SPCVD process deposits dense glass and not soot. Unlike outside vapor deposition (OVD), this prevents the

loss of volatile components such as fluorine. The plasma environment creates a unique chemistry by ionizing the feed stock materials in the plasma. SPCVD also allows for the incorporation of nitrogen whose effects on Er^{3+} provides an advantage by placing the rare earth in a high field environment.

Wide Er fluorescence emission up to 55 nm FWHM has been achieved in crucible melted glasses, but crucible melting has not produced fibers with losses below 100 dB/km. SPCVD makes high fluorine content glasses with high purity and low loss (<5 dB/km) thereby achieving the width of a crucible melted glass with the low-loss of CVD glass.

SiO_2 is the main component of the glass to maintain compatibility with existing fibers and processing. Al_2O_3 additions of greater than 3 wt% considerably broaden the Er^{3+} emission, while F additions fill in the 1540 nm region and further broaden the Er^{3+} emission envelope.

Preferably, the amount of F plus N ranges from 2.5 to 5.0 wt.%. The preferred embodiment contemplates only F, only N or the presence of both F and N.

Doping the glasses with a rare earth metal is desirable for enhancing the emission and absorption spectra, as discussed above. Therefore, the glasses of the present invention include an oxide of a rare earth element, such as Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu. Preferably, the rare earth element is Er, Pr, Eu, or Dy. Even more preferably, the rare earth element is Er (e.g., Er_2O_3).

The glasses also may contain various other components. For example, the glasses may further include 0-5 wt.% of other oxides, such as Ta_2O_5, B_2O_3, SnO, ZrO_2, P_2O_5, Sb_2O_5, As_2O_3 or Bi_2O_3.

All optical amplifiers, and particularly erbium doped fiber amplifiers have experienced explosive deployment in fiber optic telecommunication systems because of the well recognized advantages that these types of devices have over repeater type amplification schemes. For example, the erbium doped fiber amplifier (EDFA) conveniently operates in the preferred 1550 nm third telecommunications spectral window, has high polarization-insensitive gain, low cross talk between signals at different wavelengths, good saturation output

power, and a noise figure close to the fundamental quantum limit. The excellent noise characteristics potentially allow hundreds of amplifiers to be incorporated along the length of a fiber telecommunications link which could then span thousands of kilometers. Optical amplifiers, and particularly EDFAs in contrast to electronic repeaters, are also transparent to data rate, signal format and wavelength over a limited range, making them especially useful for wavelength multiplexed communication systems that simultaneously transmit a large number of signals using different wavelength bands for each signal.

Example I

Fig. 1 shows the normalized Er^{3+} emission intensity as a function of wavelength. The emission spectra of Er^{3+} in pure SiO_2 (curve I) is the narrowest. The additions of fluorine (curve II) and Al_2O_3 (curve III) significantly broaden the emission from 23 nm to 28 and 44 nm FWHM respectively. Losses of less than 2 dB/km have been achieved in both systems. By combining F and Al_2O_3, the width is further increased to 50 nm (curve IV). By adding appropriate glass modifiers such as CaO and Ta_2O_5 or K_2O and Sb_2O_3 emission FWHM in excess of 55 nm can be achieved. Curve V shows the Er^{3+} fluorescence from a $CaO\text{-}Ta_2O_5\text{-}Al_2O_3\text{–}SiO_2$ glass

Fig. 2 shows that F, N and Er can be simultaneously doped into the preform. The N^{3-} anion has a high charge that significantly alters the amplification characteristics. The combination of F and N also are beneficial since one F- and one N^{3-} can substitute for two O^{2-} to form a pseudo-oxide structure.

Example II (Prior Art)

Al_2O_3 doping is currently used in Type II EDFA to both increase the Er_{3+} solubility and gain flatness over pure SiO_2. However, these compositions can only yield a 40 nm band gain ripple of 30% and are prone to devitrification at high levels of Al_2O_3, greater than a few wt%. The inventive glasses yield a 40 nm band gain ripple of less than 20% and are therefor more desirable for multichannel EDFA's.

Fluoride glasses such as ZBLAN ($53ZrF_4$-$20BaF_2$-$4LaF_3$-$3AlF_3$-$20NaF$ in mole %) are also known for their gain flatness and low phonon energy. They must be pumped at 1480 nm due to upconversion, and as a result of the 1480 pumping, they have increased noise. They also are extremely difficult to fiberize, are not fusion sliceable, are prone to devitrification and have poor durability.

These glasses provide a means for producing low-loss rare earth doped fiber with improved gain flatness for increased channel capacity. Fiber produced by this method is fusion spliceable, compatible with existing draw methods and applicable to both fiber and planar amplifiers.

The invention includes making such rare earth doped surface plasma chemical vapor deposition fluorine doped glasses by plasma depositing dense high purity glass wherein loss of volatile glass components is inhibited. A plasma is created and the plasma environment is utilized to ionize the glass component feed stock materials which react and form a dense glass deposit while inhibiting the loss of volatile components, such as fluorine. In addition to providing rare earth doped glasses that have beneficial fluorine levels and fluorine glass compositions since the volatile loss of the volatile fluorine component is inhibited. The invention also includes incorporating nitrogen into such glasses by nitrogen doping using the reactive plasma environment. The making of such rare earth doped surface plasma chemical vapor deposited fluorine doped glasses includes the making of optical waveguide amplifier glass by plasma chemical deposition of rare earth fluorine doped light amplication glass by inhibiting the volatile loss of volatile glass components such as fluorine. Such plasma deposition includes providing beneficial high purity fluorine doped oxide glass chemistry which results in beneficial optical amplification properties such as low loss < 100dB/km; ≤ 5dB/km in the 1550 nm wavelength region and broad Er^{3+} emission spectra with FWHMs greater than 44 nm and 40 nm Er^{3+} band gain ripple less than 20%.

In addition to these embodiments, persons skilled in the art can see that numerous modifications and changes may be made to the above invention without departing from the intended spirit and scope thereof.

WE CLAIM:

1. A rare earth doped surface plasma chemical vapor deposition fluorine doped glass comprising:

Component	Weight Percent
SiO_2	0-95
GeO_2	0-95
Al_2O_3	0-15
Ga_2O_3	0-15
F	2-10
N	0-10
R_2O_3	0.01-2.0

with a SiO_2 + GeO_2 range from 80-95 wt.%, an Al_2O_3 + Ga_2O_3 range from 5-15 wt.%, and R_2O_3 is a rare earth oxide, wherein the fluorine doped glass is a high purity deposited dense glass in which volatile loss of fluorine is prevented.

2. A glass according to claim 1 wherein F and N range from 2.5 to 5.0 wt.%.

3. A glass according to claim 1 wherein said glass has a 1550 nm loss < 100 dB/km.

4. A glass according to claim 1 containing at least 3 weight percent Al_2O_3.

5. A glass according to claim 1 wherein R_2O_3 is a rare earth oxide of Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu.

6. A glass according to claim 1 wherein R is a rare earth oxide of Er, Pr, Eu or Dy.

7. A glass according to claim 1 wherein R_2O_3 is Er_2O_3.

8. A glass fiber suitable for use as an optical fiber amplifier comprising the glass of claim 3.

9. An optical amplifying device comprising the glass fiber of claim 8.

10. An electrical optical device made from the glass of claim 1.

11. A rare earth erbium and fluorine doped surface plasma chemical vapor deposition glass comprising:

Component	Weight Percent
SiO_2	0-95
GeO_2	0-95
Al_2O_3	3-15
Ga_2O_3	0-12
F	2-10
N	0-10
R_2O_3	0.01-2.0

with a SiO_2 + GeO_2 range from 80-95 wt.%, an Al_2O_3 + Ga_2O_3 range from 5-15 wt.%, and R_2O_3 is Er_2O_3, wherein the glass is a high purity deposited dense fluorinated glass formed from an ionizing plasma wherein a loss of volatile components is prevented.

12. A glass according to claim 1 wherein said glass has a 1550 nm loss < 100 dB/km and an Er^{3+} emission spectra with a FWHM > 44 nm.

13. A glass according to claim 1 wherein said glass has a 1550 nm loss < 5 dB/km and an Er^{3+} emission spectra with a FWHM ≥ 50 nm.

14. A glass according to claim 1 wherein said glass has a 1550 nm loss < 5 dB/km and an Er^{3+} emission spectra with a FWHM ≥ 55 nm.

15. A glass according to claim 1 wherein said glass has a 40 nm Er^{3+} band gain ripple less than 20%.

16. A glass according to claim 13 wherein said glass has a 40 nm Er^{3+} band gain ripple less than 20%.

17. A glass according to claim 1 wherein said glass is simultaneously doped with F, N and Er with a F^- and a N^{3-} substituting for oxygen to form a pseudo-oxide glass structure.

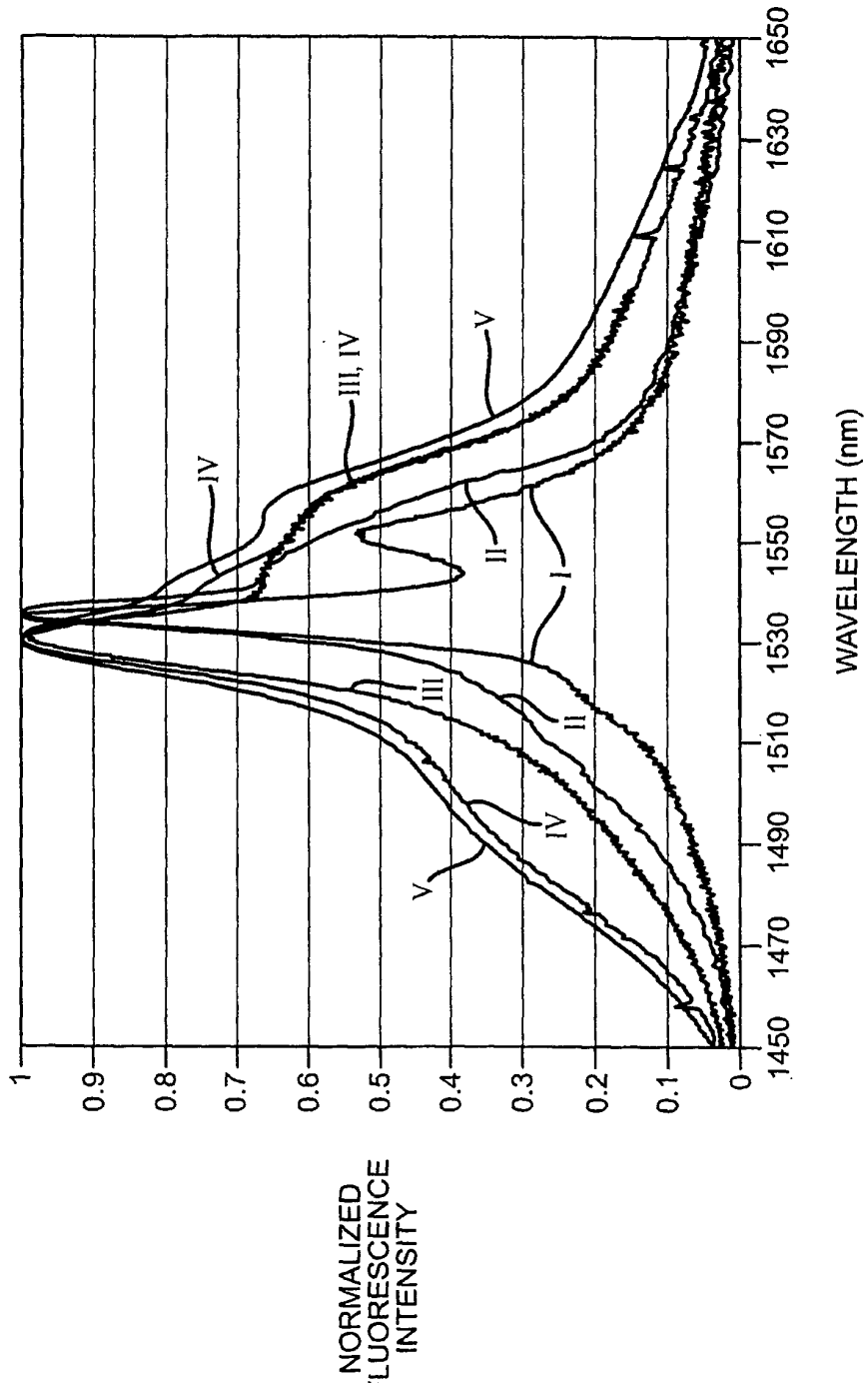
18. An optical amplifier comprising a glass of claim 16.

19. An optical amplifier comprising a glass of claim 11, said glass having a 1550 nm loss < 5 dB/km, an Er^{3+} emmission spectra with a FWHM > 44 nm and a 40 nm Er^{3+} band gain ripple less than 20%.

20. A method of making a rare earth doped glass that includes providing rare earth dopant feedstocks and fluorine feedstocks, forming a reaction plasm, ionizing the feedstocks in the plasma and depositing a dense rare earth fluorine doped glass wherein the loss of volatile fluorine is prevented.

21. A method of making a rare earth doped optical waveguide amplifier glass with a broad Er^{3+} emission spectra FWHM > 44nm and 1550 nm loss < 100 dB/km, that includes providing rare earth dopant feedstocks and fluorine feedstocks, forming a reaction plasm, ionizing the feedstocks in the plasma and depositing a dense rare earth fluorine doped glass wherein the loss of volatile fluorine is prevented.

FIG. 1


NORMALIZED FLUORESCENCE INTENSITY
WAVELENGTH (nm)
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0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1450
1470
1490
1510
1530
1550
1570
1590
1610
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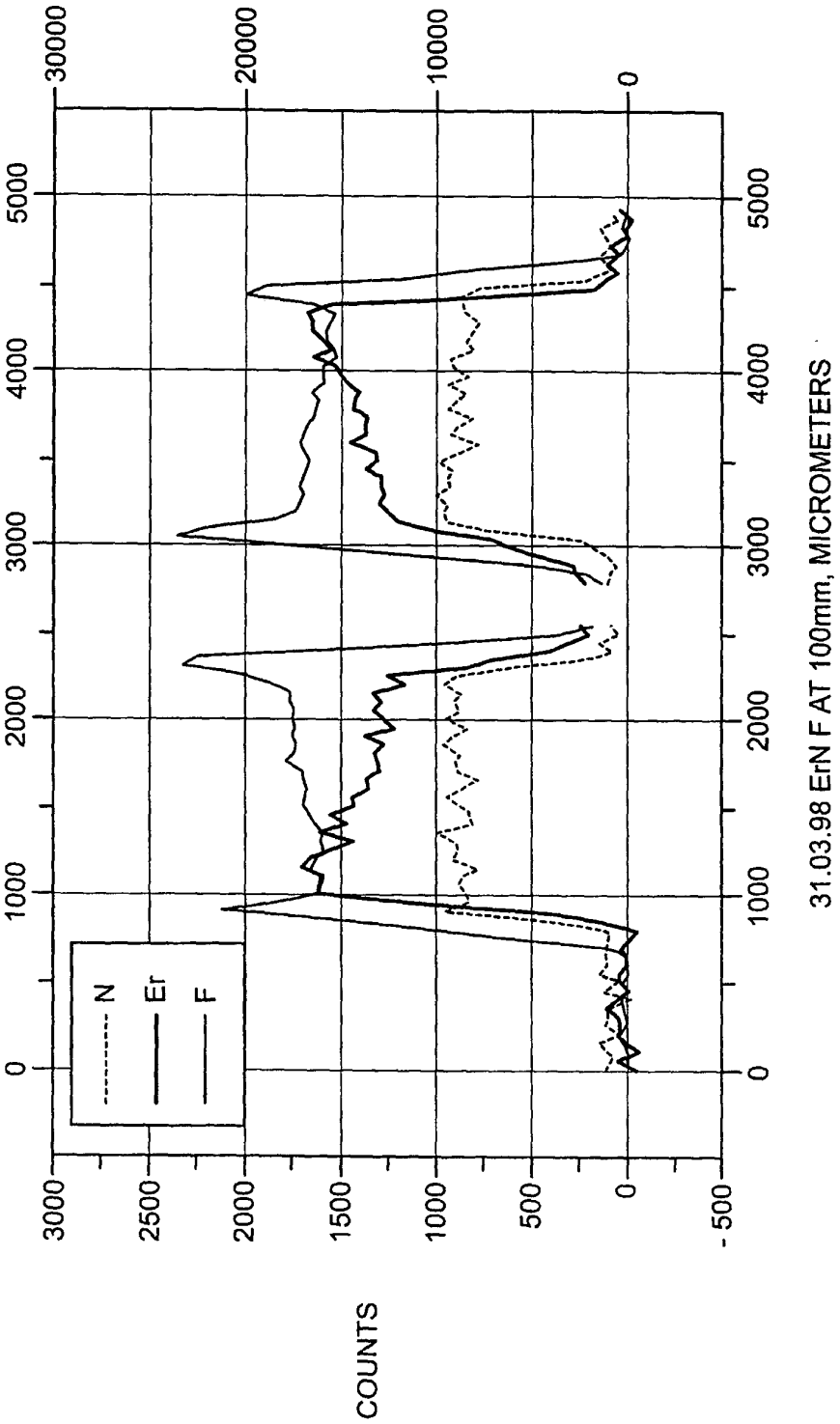
1650
I
II
III
IV
V
III, IV

FIG. 2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20000
10000
0
5000
4000
3000
2000
1000
0
N
Er
F
3000
2500
2000
1500
1000
500
0
- 500
COUNTS
31.03.98 ErN F AT 100mm, MICROMETERS

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03602

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C03C 3/04; H05H 1/24; H01S 3/17

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 359/341; 427/569, 576, 578, 579, 163.2; 501/37, 42, 43, 54, 57, 64, 68, 73

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,798,306 A (DICKINSON, JR) 25 AUGUST 1998.	1-19
A	WO 98/58884 A (CHU et al.) 30 DECEMBER 1998.	1-19
A	JP 04092825 A (TANAKA et al.) 25 MARCH 1992.	1-21

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03602

A. CLASSIFICATION OF SUBJECT MATTER:
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